(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 199940129 B2
(10) Patent No. 747821

(54) Title
Anti-hydrating and sulfur-resistant catalyst for CO-shift process and preparation method thereof

(51)6 International Patent Classification(s)
B01J 023/882

(21) Application No: 199940129

(22) Application Date: 1999 .07 .15

(30) Priority Data

(31) Number	(32) Date	(33) Country
98110348	1998 .07 .15	CN

(43) Publication Date : 2000 .02 .10
(43) Publication Journal Date : 2000 .02 .10
(44) Accepted Journal Date : 2002 .05 .23

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(56) Related Art
JP 8176034
US 4153580

Anti-hydrating and Sulfur-resistant Catalyst for CO-Shift Process and Preparation Method Thereof

Abstract

The invention relates to a sulfur-resistant catalyst for Co shift process and the preparation method thereof, comprising cobalt and magnesium compounds as active components, an alkali metal compound as promoter, a porous aluminum compound and a porous magnesium compound or the combination thereof as the skeletal material of the carrier, and one or more compounds selected from the group of rare earth metal compounds, especially nitrates thereof, and zinc compounds as the anti-hydration assistant, and the titanium compound, wherein the content of said titanium compound in the carrier is controlled in the range of 30~80 wt % based on mass percent and calculated as titanium dioxide; and the preparation method as described in the specification.

S & F Ref: 472725

AUSTRALIA

PATENTS ACT 1990

COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title:	Anti-hydrating and Sulfur-resistant Catalyst for CO-Shift Process and Preparation Method Thereof

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

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Anti-hydrating and Sulfur-resistant Catalyst for CO-Shift Process and Preparation Method thereof

The present invention relates to a new sulfur-resistant catalyst for CO-shift process and the preparation method thereof, and more particularly, relates to an anti-hydrating and sulfur-resistant catalyst for the shift process and the preparation method of the catalyst.

Shift reaction has been known as an important method for producing hydrogen and synthesis gas. For raw materials with high sulfur content, a sulfur-resistant catalyst should be applied in the shift reaction. At present, the widely used sulfur-resistant catalysts for low temperature shift process in industry mostly consist of γ-Al_2O_3 or γ-Al_2O_3 modified by rare earth as their carriers. The Chinese Patent CN1018049 disclosed a catalyst consisting of γ-Al_2O_3 as its carrier, Mo and Co as active components and alkali metals as activity promoter; said catalyst should be sulfurized at relatively high temperature before use. U.S.Patent 4,153,580 teaches that the rare earth oxides were added to the hydrated alumina and the admixture was blended together, formed into the desired shape, calcinated to obtain a carrier and impregnated it with desired amounts of the decomposable cobalt and molybdenum compounds, which, after calcination, were resolved into oxides, thus a sulfur-resistant shift catalyst was obtained. Although this catalyst could be easily sulfurized at a lower temperature, it showed poor ability for preventing hydration, just as the one described in the Chinese Patent CN1018049 , that is, when used under a high steam partial pressure, these catalyst would be subject to hydration reaction in a certain extent, resulting in phase changes and deactivation of the catalytic. To stabilize the structure of the catalysts used under high steam partial pressure, a carrier consisting of MgO, Al_2O_3 and TiO_2 and the rare earth compounds as activity promoter proposed in the Chinese Patent CN1096494, which has better solved the problem of hydration. This catalyst is classified, as non-alkali metal sulfur-resistant shift catalyst for it does not contain alkali metal compounds in its preparation. Unfortunately, however, the cost is relatively high for producing this catalyst because of the beating and kneading processes. In the Chinese Patent CN1154271 (application No. 96100935.7) a cost-effective method is described, which consists of blending in dry state, kneading, calcinating and impregnating. The main components of the catalyst carrier prepared by this patent are MgO and Al_2O_3, with a small amount of TiO_2.

The catalyst prepared by this method showed high strength, high stability and good regeneration performance which may be the result of the formation of spinel structure during calcination of MgO and Al_2O_3. The addition of alkali metal compounds in the preparation contributes to the good activity of the catalyst at low temperature, but its anti-hydratability is poor.

At present, in the projects of "substituting oil with coal" as feedstocks in large-scale fertilizer plants and the expansion and revamping of production facilities of medium-scale plants, most of them have been designed to choose coal as raw material, 4.0MPa gasification unit , three-stage sulfur-resistant shift process (medium temperature shift in series with low temperature shift) and followed by methanation purification. In such process of low-temperature shifting technology, the catalyst must be operated under the severe conditions of high pressure, high steam partial pressure and low temperature, which is often in the range of not more than 20℃ from the dew point. That means the sulfur-resistant shift catalyst should possess not only good activity at low temperature but also good anti-hydrat ability as well as structural stability.

The aim of the present invention is to provide a catalyst having good anti-hydratability, low temperature activity and structural stability, and is free from hydration and phase change when it is used under the severe conditions mentioned above.

The sulfur-resistant conversion catalyst according to the present invention comprises cobalt and molybdenum compounds as active components , an alkali metal compound as a promoter, a porous aluminum compound, a porous magnesium compound or the combination thereof as the skeletal materials of the carrier, and one or more compounds selected from the group of rare-earth metal compounds, preferably nitrates thereof, and zinc compounds, preferably zinc oxide and zinc nitrate, as an anti-hydrating assistant in combination with a titanium compound , wherein the content of the titanium compound in the carrier is controlled preferably in the range of 30wt% ～ 80wt%, calculated as TiO_2 , thus a sulfur-resistant catalyst for CO-shift process is unexpectedly obtained having excellent anti-hydratability, good low temperature activity

and structural stability.

The contents of the cobalt and molybdenum compounds as the active components in the catalyst are MoO_3 5wt%~20wt% and CoO 0.5wt% ~5wt%, and the content of the alkali metal promoter in the catalyst is 0.1wt%~20wt% (calculated as oxides), said alkali metal may be potassium or sodium. As for the selection of the percent range of active components and the alkali metal promoter, see the Chinese Patent CN1018049, CN1042482 and CN1048989.

Said porous aluminum compounds used as the skeletal material in the invention may be aluminum hydroxide, pseudoboehmite, gibbsite or alumina, preferably aluminum hydroxide or pseudoboehmite. Said porous magnesium compounds of the invention may be magnesium hydroxide, magnesium carbonate, magnesium oxide, magnesium nitrate, preferably magnesium carbonate or magnesium oxide. The combination of any two or more compounds mentioned above may also be used as the skeletal material.

Said zinc compounds may be zinc oxide or heat-decomposable zinc compounds such as zinc nitrate, zinc carbonate, and the like, which can be decomposed into zinc oxide when being heated. Said anti-hydration assistant used in the invention may be nitrates or oxides of lanthanum, nitrates or oxides of cerium, zinc nitrate and zinc oxide and the like, or the mixture of any two or more compounds mentioned above, preferably lanthanum nitrate, lanthanum oxide or zinc nitrate.

If a rare earth compounds is used as the anti-hydration assistant, its content should be 0.01wt%~10wt% of the total weight of the calcined carrier, calculated as oxides.

If zinc compound is used as the anti-hydration assistant, its content should be preferably 0.10wt%-10wt%t of the total weight of the calcined carrier, calculated as oxides .

The content of the titanium compound calculated as titanium dioxide is preferably in the range of 30wt% ~ 80wt% of total weight of the calcined carrier.

The titanium compounds used in the present invention may be titanium

dioxide, titanium hydroxide, metatitanic acid, titanium tetraoxide, rutile or anatase or the mixture of any two or more substances thereof, preferably metatitannic acid.

The preparation process of the carrier of the catalyst of the present invention is illustrated as follows. Said porous aluminum compounds and porous magnesium compounds are mixed with the anti-hydration assistant selected from one or more of said rare earth metal compounds, preferably nitrates thereof, and said zinc compounds, preferably zinc oxide and zinc nitrate, then the resultant mixture is decomposed by calcination, and crushed; subsequently the resultant mixture is mixed in dry state with the titanium compound, and the resultant blend is extruded and calcined to obtain the carrier of the catalyst; a co-impregnation solution is prepared by mixing the molybdenum and cobalt compounds as the active components and the alkali metal compound, and the obtained carrier is impregnated with the resultant co-impregnation solution, then the impregnated carrier is calcined and decomposed to obtain the anti-hydrating and sulfur-resistant conversion catalyst of the present invention .

A peptizer can be added while the mixture mentioned above and the titanium compound are mixed. Said peptizer may be nitric acid, the aqueous solution of nitrates of alkali earth metals, the aqueous solution of nitrates of alkali metals, the aqueous solution of sulphates of alkali metals, or the solution of any two or more mixtures thereof, preferably nitric acid or the solution of potassium nitrate. Said peptizer may also be a solid peptizer, such as oxides of alkali earth metals, hydroxides of alkali earth metals or sulfides of alkali earth metals.

When the sulfur-resistant conversion catalyst of the present invention is used under a severe condition of 20℃ below dew point, no hydration and no phase change happen to the catalyst, showing that the catalyst has higher anti-hydratability and structural stability, but when the commercial catalysts for low temperature conversion, e.g. $C_{25-2-02}$, QCS-02 and EB-4 and the like are used under the same conditions, they all suffer from phase change (see

appended Fig. 1). Furthermore, the preparation process of the catalyst according to the present invention is simple, as the beating and kneading process are exempted , the production cost can be reduced significantly.

The following is intended for illustrating further the present invention in combination with the examples and appended drawings, but the following examples shall not be construed as limiting the scope of the invention.

Fig 1. shows a phase change diagram before and after the hydrothermal treatment of the catalyst CT-4 of the invention, wherein a: before hydrothermal treatment; b: after hydrothermal treatment.

Fig 2. shows a phase change diagram before and after the hydrothermal treatment of several commercial and conventional catalysts, wherein a: fresh commercial catalyst EB-4; b: fresh commercial catalyst QCS-02; c: fresh commercial catalyst $C_{25\text{-}2\text{-}02}$; d: commercial catalyst EB-4 after hydrothermal treatment; e: commercial catalyst QCS-02 after hydrothermal treatment; f: commercial catalyst $C_{25\text{-}2\text{-}02}$ after hydrothermal treatment.

Fig 3. shows a phase spectrum after hydrothermal treatment of the catalysts according to the present invention, wherein a: CT-1 after hydrothermal treatment; b: CT-2 after hydrothermal treatment; c: CT-3 after hydrothermal treatment; d: CT-4 after hydrothermal treatment.

Example 1: Preparation of the catalyst

(1)Preparation of the carrier

Carrier Z-1

A solution was prepared with 10g of La_2O_3, and mixed with 200g of $Al(OH)_3$ and 100g of $MgCO_3$. The resultant blend was calcined at 700℃for 2 hours and the calcined product was crushed; 400g of metatitanic acid was added to the crushed product, then 10% nitric acid was added; the resultant mixture was kneaded and extruded and the extruded bars were calcined at 500 ℃. Eventually the catalyst carrier was obtained and marked as carrierZ-1. Its composition is shown in Table 1.

Carrier Z-2

The preparation procedures were same as those for Carrier Z-1, except that the aqueous solution containing 30g of zinc nitrate was used instead of the aqueous solution of La_2O_3. The catalyst carrier obtained was marked as Carrier Z-2. Its composition is shown in Table 1.

Carrier Z-3

The preparation procedures were same as those for Carrier Z-1, except that 200g of metatitanic acid was used instead of 400g of metatitanic acid and that the weight of $MgCO_3$ used was Og instead of 100g. The catalyst carrier obtained was marked as Carrier Z-3. Its composition is shown in Table 1.

Carrier Z-4

The preparation procedures were same as those for Carrier Z-2, except that 200g of metatitanic acid was used instead of 400g of metatitanic acid. The catalyst carrier obtained was marked as Carrier Z-4. Its composition is shown in Table 1.

Carrier Z-5

The preparation procedures were same as those for Carrier Z-1, except that 36g of La_2O_3 was used instead of 10g of La_2O_3 , the weight of $Al(OH)_3$ used was Og instead of 200g, and 200g of titanium hydroxide and 200 g of metatitanic acid were used instead of 400 g of metatitanic acid used in Z-1. The catalyst carrier obtained was marked as Carrier Z-5. Its composition is shown in Table 1.

Carrier Z-6

The preparation procedures were same as those for Carrier Z-2, except that

the weight of zinc nitrate used was 90g, 100g of MgO was used instead of 100g MgCO3, and the weight of metatitanic acid used was 200g. The catalyst carrier obtained was marked as Carrier Z-6. Its composition was shown in Table 1.

Carrier Z-7

The preparation procedures were same as those for Carrier Z-1, except that the weight of La_2O_3 used was 0.05g. The obtained catalyst carrier was marked as Carrier Z-7. Its composition is shown in Table 1.

Carrier Z-8

The preparation procedures were same as those for Carrier Z-2, except that the weight of zinc nitrate used was 1g. The obtained catalyst carrier was marked as Carrier Z-8. Its composition is shown in Table 1.

(2)Preparation of the catalyst

A co-impregnation solution was prepared with 55g of ammonium molybdate, 5.0g of cobalt nitrate and 50g potassium carbonate, then 50g of each of the carriers obtained as mentioned above was impregnated respectively in said co-impregnation solution, then calcined and decomposed under 400℃, to obtain the catalysts which are marked as CT-1, CT-2, CT-3, CT-4, CT-5, CT-6 CT-7 and CT-8 correspondingly.

Example 2 Performance test of the catalyst

In a pressurized evaluation apparatus packed with the original grains of the catalyst, the catalysts of the present invention and the commercial catalysts were treated hydrothermally in a medium consisting of hydrogen and steam at a temperature which was 18～20℃ apart from the dew point (i.e. pressure:

4.0 MPa, temperature: 220～222℃, space velocity: 2000h^{-1}, and a water/gas ratio: 0.7) for 72 hours, then phase changes of the catalysts were determined. The results are shown in Figs. 1, 2 and 3. From Fig. 1 and Fig. 2, it can be seen that no phase change occurred basically and no hydration peaks appeared after hydrothermal treatment of the catalyst CT-4 of the invention. This demonstrates that no hydrated aluminum hydroxide was formed after hydrothermal treatment, but for all the commercial catalysts $C_{25-2-02}$, QCS-02 and EB-4, the hydration peaks (i.e. the peaks appearing between 10° ～ 20°) appeared after hydrothermal treatment, showing the occurrence of hydration of these catalysts. From Fig. 3, it can be seen that no hydration occurred and no hydration peaks formed for all the catalysts CT-1, CT-2, CT-3 and CT-4 of the present invention after hydrothermal treatment.

Then, the strength of each fresh sample, boiled sample and hydrothermally treated sample of the catalysts of the present invention and the commercial catalysts was measured respectively. Data obtained are shown in Table 1, from which it can be seen that each of the catalysts of the present invention has not only superior initial strength to that of the commercial catalyst $C_{25-2-02}$, but also higher strength retention rate after being boiled or hydrothermally treated, showing that the catalysts of the present invention have excellent strength stability.

Example 3 <u>Running test of the catalysts</u>

A simulation evaluation of the catalyst CT-4 of the invention was carried out under the following conditions, and the results are shown in Table 3.

Evaluation conditions: the amount of catalyst loaded was 50 ml, and was diluted with α-Al_2O_3 beads to a total volume of 100 ml in a volume ratio of α-Al_2O_3 bead/catalyst of 1 : 1.

Sulfurization conditions: pressure: 1.5Mpa, temperature: 260℃, space velocity: $1000h^{-1}$, and sulfurizing time: 20 hr.

Table 1

Carrier No.	TiO_2, wt.%	La_2O_3, wt.%	ZnO, wt.%	MgO, wt.%	Al_2O_3, wt.%
Z-1	63.3	1.9		9.3	25.4
Z-2	62.9		2.5	9.3	25.3
Z-3	53.4	3.3			43.3
Z-4	45.7		3.6	13.6	37.1
Z-5	78.2	9.4		12.4	
Z-6	37.4		9.0	23.2	30.4
Z-7	64.3	0.01		9.6	26.1
Z-8	64.3		0.09	9.6	26.1

Table 2

Item \ Catalyst		Strength of catalyst of the invention (N/cm)				Commercial catalyst (N/cm)
		CT-1	CT-2	CT-3	CT-4	$C_{25-2-02}$
Fresh catalyst		126	129	134	136	86
Boiled catalyst	Strength	108	116	119	120	64
	Retention rate%	85.7	89.9	88.8	88.2	74.4
Hydrothermally treated catalyst	Strength	114	112	118	116	67
	Retention rate%	90.5	85.7	88.1	85.3	77.9

Table 3

Pressure (MPa)	Space velocity (h^{-1})	Ratio of water/gas	T_{inlet} (℃)	CO % (Vol)		CO shift (%)
				Inlet	Outlet	
1.5	1000	1.0	260.6	5.89	0.47	91.58
3.8	3000	0.76	260.0	5.49	0.36	93.11
3.8	2000	0.76	260.1	5.41	0.27	94.75
3.8	2000	0.63	260.0	5.41	0.30	94.16
3.8	2000	0.63	220	5.20	0.34	93.14
3.8	2000	0.63	215	5.29	0.30	94.04
3.8	2000	0.63	210	5.16	0.28	94.31
3.8	2000	0.63	210	3.77	0.20	94.51
3.8	2000	0.63	210	1.67	0.10	94.52
3.8	2000	0.63	205	3.44	0.21	93.69

The claims defining the invention are as follows:

claims:

1. A sulfur-resistant shift catalyst, comprising cobalt and molybdenum compounds as the active components, an alkali metal compound as a promoter, a porous aluminum compound, a porous magnesium compound or a combination thereof as the skeletal material of the carrier of the catalyst, one or more compounds selected from the group consisting of rare earth metal compounds and zinc compounds as the anti-hydration assistant, and a titanium compound, wherein the content of titanium compound is in the range of 30 wt%～80 wt% on the basis of the total weight of the calcined carrier, calculated as titanium dioxide .

2. The catalyst according to claim 1, wherein the contents of said cobalt compounds and molybdenum compound as the active components of the catalyst are MoO_3 5 wt%～20 wt%, CoO 0.5 wt%～5 wt% on the basis of the total weight of the catalyst.

3. The catalyst according to claim 1, wherein the content of said alkali metal promoter is 0.1 wt%-20 wt% on the basis of the total weight of the catalyst, calculated as the alkali metal oxide, and said alkali metal may potassium or sodium.

4. The catalyst according to any one of the claims 1-3, wherein the content of said rare earth metal compounds is 0.01 wt%～10 wt% of the total weight of the calcined carrier, calculated as the oxide.

5. The catalyst according to any one of the claims 1-3, wherein said anti-hydration assistant is one or more compounds selected from nitrates or oxides

of lanthanum, nitrates and oxides of cerium.

6. The catalyst according to any one of the claims 1-3, wherein said anti-hydration assistant is nitrates or oxides of lanthanum.

7. The catalyst according to claim 6, wherein the content of said nitrates or oxides of lanthanum is 0.01 wt%~ 10 wt% of the total weight of the calcined carried, calculated as oxide.

8. The catalyst according to any one of the claims 1-3, wherein said zinc compound is one or more compounds selected from zinc oxide and heat-decomposable zinc compounds which can be decomposed into zinc oxide when being heated.

9. The catalyst according to any one of the claims 1-3, wherein said anti-hydration assistant is zinc nitrate or zinc oxide.

10. The catalyst according to any one of the claims 1-3, wherein the content of zinc compounds is 0.10 wt%~ 10 wt% of the total weight of the calcined carrier, calculated as oxide.

11. The catalyst according to any one of the claims 1-3, wherein said titanium compound is one or more substances selected from the group consisting of titanium oxide, titanium hydroxide, metatitanic acid, titanium tetraoxide, rutile or anatase.

12. A method for preparing the sulfur-resistant catalyst for CO-shift process according to anyone of claims 1-11, comprising the following steps:

a. mixing the porous aluminum compound and/or porous magnesium compound with one or more compounds selected from the group consisting of

of rare earth metal compounds and zinc compounds as the anti-hydration assistant, and calcining the resultant mixture, then crushing the decomposed solid;

b. mixing in dry state the mixture obtained in step a) with the titanium compound, then extruding the resultant blend into bars, and calcining the extruded bars to obtain the catalyst carrier; and

c. preparing a co-impregnation solution with the molybdenum and cobalt compounds as the active components of the catalyst and alkali metal compound, impregnating the carrier obtained in step b) with the solution, then calcining and decomposing the impregnated carrier.

13. The method according to claim 12, wherein said porous aluminum compounds and magnesium compounds are one ,or more compounds selected from the group consisting of aluminum hydroxide, pseudoboehmite, gibbsite, alumina, magnesium hydroxide, magnesium carbonate, magnesium oxide and the like.

14. The method according to claim 12, wherein said anti-hydration assistant is one or more compounds selected from nitrates or oxides of lanthanum and nitrates or oxides of cerium.

15. The method according to claim 12, wherein said titanium compound is one or more substances selected from the group consisting of titanium oxide, titanium hydroxide, metatitanic acid, titanium tetraoxide, rutile and anatase.

16. The method according to claim 12, wherein the content of said

rare earth metal compound is 0.01wt%-10wt% of the total weight of the calcined carrier (calculated as oxide).

17. The method according to claim 12, wherein the content of said zinc compound is 0.1wt%-10wt% of the total weight of the calcined carrier (calculated as oxide).

18. The method according to claim 17, wherein said zinc compound is one or more compounds selected from zinc oxide and heat-decomposable zinc compounds which can be decomposed into zinc oxide when being heated.

19. The method according to claim 17, wherein said zinc compound is zinc nitrate or zinc oxide.

20. The method according to claim 12, wherein said rare earth metal compounds are nitrates or oxides of lanthanum.

21. A sulfur-resistant shift catalyst, substantially as hereinbefore described with reference to any one of the examples.

22. A method for preparing a sulfur-resistant shift catalyst, said method being substantially as hereinbefore described with reference to any one of the examples.

Dated 15 July, 1999
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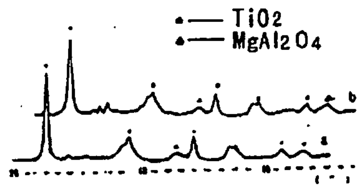

FIG. 1

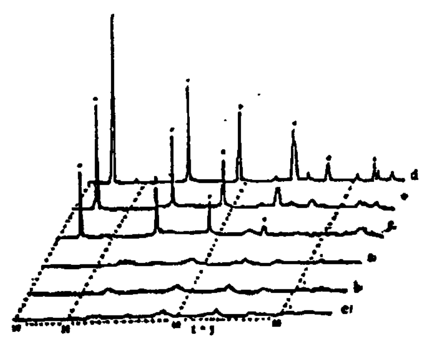

FIG. 2

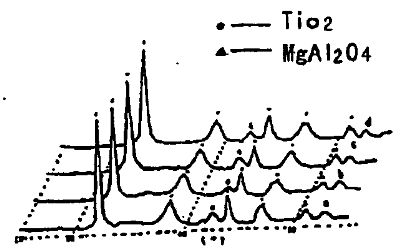

FIG. 3